

Process for Producing Cyclopropanecarboxylates

Field of the Invention:

The present invention relates to a process for producing
5 cyclopropanecarboxylates.

Background of the invention

There have been known a production method of carboxylic acid ester from a carboxylic acid and an alcohol using a protonic acid catalyst. A production method using sulfuric acid as a catalyst is disclosed (Japanese Patent Laid-Open Publication No. 9-188649), and also disclosed is a method of using p-toluenesulfonic acid as a catalyst (Japanese Patent Laid-Open Publication No. 11-228491).

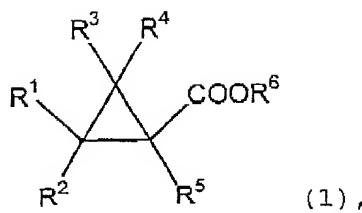
15 However, the methods using mineral acid or organic acid having strong acidity cause significant coloring due to a side reaction, which has made these methods not necessarily efficient as industrial production methods.

20 Summary of the Invention

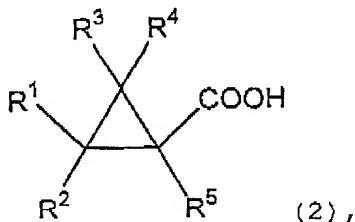
According to the present invention, a cyclopropanecarboxylate can be conveniently produced, through dehydration reaction, from a cyclopropanecarboxylic acid and an alcohol in the presence of the catalyst as defined below.

25 The present invention provides

a process for producing a cyclopropanecarboxylate of formula (1):



which process comprises reacting
a cyclopropanecarboxylic acid of formula (2):



5 with a monohydroxy compound of formula (3):



in the presence of

10 a compound comprising an element of Group 4 of the Periodic
Table of Elements,

wherein in formula (1) and (2),

R^1 , R^2 , R^3 , R^4 , and R^5 independently represent
a hydrogen atom, a halogen atom,

15 an alkyl group which may be substituted,
an alkenyl group which may be substituted,
an alkynyl group which may be substituted,
an aryl group which may be substituted; and
in formula (3),

20 R^6 represents
an alkyl group which may be substituted, or
an aryl group which may be substituted.

Detailed Description of the Invention

The halogen atom or the term "halo" in the present specification means a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom in R¹ through R⁶.

The alkyl group which may be substituted and the alkenyl group which may be substituted may be linear, branched, or cyclic.

The term alkenyl or alkynyl in R¹ through R⁶ and substituents that may be present therein means the same group as specified for R¹ to R⁵ below.

The aryl group represented by R¹ through R⁶ and the "aryl" including those present as the substituent group as in aryloxy, or haloaryloxy includes a (C₆-C₁₄)aryl group such as phenyl, biphenyl, naphthyl, anthracenyl or the like.

R¹, R², R³, R⁴, and R⁵ in the cyclopropanecarboxylic acid (2) and the cyclopropanecarboxylate (1) will be explained below.

Examples of the alkyl group which may be substituted represented by R¹, R², R³, R⁴, or R⁵ include, for example, a (C₁-C₁₀)alkyl group such as methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, menthyl and the like.

Examples of the alkenyl group which may be substituted represented by R¹, R², R³, R⁴, or R⁵ include, for example, a (C₂-C₅)alkenyl group such as vinyl, 1-methylvinyl, 1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 3-methyl-2-butenyl or the like.

The alkyl group, alkenyl and alkynyl groups represented by R¹, R², R³, R⁴, or R⁵ may be independently substituted with at least one member selected from

a halogen atom, an alkoxy group, an alkoxy carbonyl group,
a haloalkoxy carbonyl group, an aryl group,
a halocycloalkylidene group, an alkoxyimino group,
an alkylsulfonyl group, an alkylsulfonyloxy group, and
5 a hydroxysulfinyl group.

Examples of the alkenyl group substituted with halogen include, a halo(C₂-C₅) alkenyl group such as 2,2-dichlorovinyl,
2,2-dibromovinyl, 2-chloro-2-fluorovinyl,
2-chloro-2-trifluoromethylvinyl,
10 2-bromo-2-tribromomethylvinyl, or the like.

Examples of the alkynyl group which may be substituted includes a propargyl group and the like.

Examples of the alkoxy group include, for example,
a (C₁-C₄) alkoxy group such as methoxy, ethoxy, n-propoxy,
15 i-propoxy, n-butoxy, sec-butoxy, or tert-butoxy group or the like.

Examples of the alkoxy carbonyl group include, for example,
a (C₁-C₄) alkoxy-carbonyl such as methoxycarbonyl,
ethoxycarbonyl, n-propoxycarbonyl, i-propoxycarbonyl,
20 n-butoxycarbonyl, sec-butoxycarbonyl, tert-butoxycarbonyl or the like.

Examples of the haloalkoxy carbonyl group include, for example, a halo(C₁-C₄) alkoxy-carbonyl group such as a 2,2,2-trifluoro-1-(trifluoromethyl)ethoxycarbonyl group or
25 the like.

Preferred aryl group are phenyl, 1-naphthyl, and 2-naphthyl groups and the like.

Examples of the halocycloalkylidene group include, for example, a halo(C₃-C₅) cycloalkylidene group such as

difluorocyclopropylidene group or the like.

Examples of the alkoxyimino group include, for example, a (C1-C3)alkoxy-imino group such as methoxyimino, ethoxyimino, an n-propoxyimino or the like.

5 Examples of the alkylsulfonyl group include, for example, a (C1-C4)alkylsulfonyl group such as methylsulfonyl, ethylsulfonyl, n-propylsulfonyl, i-propylsulfonyl, tert-butylsulfonyl or the like.

10 Examples of the alkylsulfonyloxy group include, for example, a (C1-C4)alkylsulfonyloxy group such as methylsulfonyloxy, ethylsulfonyloxy, n-propylsulfonyloxy, i-propylsulfonyloxy, tert-butylsulfonyloxy or the like.

The cyclopropanecarboxylic acid (2) includes any optical isomer or mixture thereof.

15 Specific examples of the cyclopropanecarboxylic acid (2) include, for example, cyclopropanecarboxylic acid, 2-fluorocyclopropanecarboxylic acid,

2,2-dichlorocyclopropanecarboxylic acid,

2,2-dimethyl-3-(dimethoxymethyl)cyclopropanecarboxylic

20 acid,

2,2,3,3-tetramethylcyclopropanecarboxylic acid,

2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylic acid,

2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid,

25 2,2-dimethyl-3-(3-methyl-2-butenyl)cyclopropanecarboxylic acid,

2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid,

2,2-dimethyl-3-(2,2,2-trichloroethyl)cyclopropanecarboxylic

acid,

2,2-dimethyl-3-(2-chloro-2-fluorovinyl)cyclopropane-
carboxylic acid,

2,2-dimethyl-3-(2-bromovinyl)cyclopropanecarboxylic acid,

5 2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylic
acid,

2,2-dimethyl-3-(1,2,2,2-tetrabromoethyl)cyclopropane-
carboxylic acid,

10 2,2-dimethyl-3-(1,2-dibromo-2,2-dichloroethyl)cyclopropane-
carboxylic acid,

2,2-dimethyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)cyclo-
propanecarboxylic acid,

2,2-dimethyl-3-{3,3,3-trifluoro-2-(trifluoromethyl)-1-
propenyl)cyclopropanecarboxylic acid,

15 2,2-dimethyl-3-(2-phenyl-1-propenyl)cyclopropanecarboxylic
acid,

2,2-dimethyl-3-(2-phenylvinyl)cyclopropanecarboxylic acid,

2,2-dimethyl-3-(2-methyl-3-phenyl-2-butenyl)cyclopropane-
carboxylic acid,

20 2,2-dimethyl-3-{(2,2-difluorocyclopropylidene)methyl}-
cyclopropanecarboxylic acid,

2,2-dimethyl-3-{2-(tert-butoxycarbonyl)vinyl)cyclopropane-
carboxylic acid,

25 2,2-dimethyl-3-{2-fluoro-2-(methoxycarbonyl)vinyl}-
cyclopropanecarboxylic acid,

2,2-dimethyl-3-{2-fluoro-2-(ethoxycarbonyl)vinyl)cyclo-
propanecarboxylic acid,

2,2-dimethyl-3-{2-fluoro-2-(tert-butoxycarbonyl)vinyl}-
cyclopropanecarboxylic acid,

2,2-dimethyl-3-[2-(2,2,2-trifluoro-1-(trifluoromethyl)-ethoxycarbonyl)vinyl]cyclopropanecarboxylic acid,
2,2-dimethyl-3-(2-aza-2-methoxyvinyl)cyclopropanecarboxylic acid,

5 2,2-dimethyl-3-(4-aza-4-methoxy-3-methylbut-1,3-dienyl)-cyclopropanecarboxylic acid,

2,2-dimethyl-3-[2-(tert-butylsulfonyl)-2-(tert-butoxycarbonyl)vinyl]cyclopropanecarboxylic acid,

10 2,2-dimethyl-3-{2,2,2-tribromo-1-(methylsulfonyloxy)ethyl}-cyclopropanecarboxylic acid,

2,2-dimethyl-3-(2,2-dibromo-2-(hydroxysulfinyl)-1-(methoxy)-ethyl)cyclopropanecarboxylic acid,

2,2-dimethyl-3-{2,2,2-tribromo-1-(methylsulfonyloxy)ethyl}-cyclopropanecarboxylic acid,

15 2-methyl-2-ethyl-3-(1-propenyl)cyclopropanecarboxylic acid,
2,2-diethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid, and

2-methyl-2-phenyl-3-(2-methyl-1-propenyl)cyclopropane-carboxylic acid.

20 Preferred are 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropanecarboxylic acid, and
2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid.

25 Next a description will be made to the monohydroxy compound of formula (3).

Examples of the alkyl group, which may be substituted, represented by R⁶, include, for example,

a (C1-C10)alkyl group which may be substituted with a member selected from

a halogen atom, a cyano group, a nitro group, an alkenyl group, a haloalkenyl group, an alkynyl group, or an aryl or heterocyclic group which may be substituted with at least one member selected from

an alkyl group, a haloalkyl group,
an alkoxy group, a haloalkoxy group,
an alkoxyalkyl group,
an alkenyl group, an alkynyl group,
an aryl group, an aryloxy group,
a haloaryloxy group, an aralkyl group (e.g. (C7-C8)aralkyl such as benzyl, phenethyl),
an acyl group (e.g. (C1-C2)acyl such as formyl, acetyl),
a haloacyloxyalkyl group (e.g. trifluoroacetyloxyalkyl),
an amino group, and a halogen atom; or

R^6 represents:

20 a 1-, or 2-indanyl group which may be substituted with an alkynyl group or an aryl or heteroaryl group (e.g. 5- or 6-membered heteroaryl group such as thienyl); or
25 a cycloalkenyl group (e.g., cyclopentenyl) substituted with at least one member selected from an oxo group, an alkyl group, an alkenyl and an alkynyl group (e.g. 4-hydroxy-3-methyl-2-(2-propenyl)-2-cyclopentene-1-one, 4-hydroxy-3-methyl-2-(2-propynyl)-2-cyclopentene-1-one).

The term "alkyl" used in the alkyl, haloalkyl, and alkoxyalkyl groups as recited in the definition of R^6 and substituents thereof includes a C1-C14 alkyl group.

Examples of the (C1-C14) alkyl group include, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, n-octyl, n-nonyl, n-decyl, undecyl, dodecyl, tridecyl, tetradecyl group and the like.

Examples of the haloalkyl group include fluoroethyl, difluoroethyl, trifluoroethyl, tetrafluoroethyl and the like.

The term "alkoxy" used in the alkoxy, haloalkoxy, and alkoxyalkyl groups includes a C1-C4 alkoxy group as defined above in this specification.

Examples of the alkenyl groups as recited above include a (C2-C5) alkenyl group (e.g. vinyl, 1-propenyl, 1-methyl-2-propenyl, 1-butenyl, 2-penten-2-yl group or the like). The haloalkenyl group that may be present on the alkyl group represented by R⁶ means the same haloalkenyl group as described for the haloalkenyl group represented by R¹ to R⁵.

Examples of the alkynyl groups that may be present on the alkyl group represented by R⁶ include a (C2-C5) alkynyl group (e.g. ethinyl, propynyl, butynyl, pentynyl or the like).

Examples of the heterocyclic group which may be substituted, include, for example, a furyl group, an isoxazolyl group, a pyrrolyl group, a thiazolyl group, an imidazolidine-2,4-dione group, a 4,5,6,7-tetrahydroisoindole group, an indole group, a pyridyl group, and further specific examples thereof include a phenoxyfuryl group, a benzylfuryl group, a propargylfuryl group, a methylisoxazolyl group, a trifluoromethylthiazolyl group, a trifluoromethoxythiazolyl group, a propynylpyrrolyl group, a propynyldioxoimidazolidinyl group, a dioxotetrahydroisoindolyl group, an oxothiazolyl group,

a halopyridyl group and the like.

Examples of the aryl group which may be substituted, represented by R⁶, include an aryl group, which may be substituted with a phenyl, an alkynyl group, an acyl group, an alkyl group, 5 an alkoxy group, or a halogen atom.

The monohydroxy compound of formula (3) includes, for example, following alkyl alcohol, aralkyl alcohol, aryl alcohol and the like.

Specific examples of the alkyl alcohol include, 10 methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, n-pentyl alcohol, neopentyl alcohol, n-hexyl alcohol, n-octyl alcohol, n-decyl alcohol, and the like.

Specific examples of the alcohol compound of formula (3), 15 wherein R⁶ represents the alkyl substituted with a halogen atom include,

fluoroethyl alcohol, difluoroethyl alcohol, trifluoroethyl alcohol, and tetrafluoroethyl alcohol.

Specific examples of the alcohol compound of formula (3), 20 wherein R⁶ represents a methyl group substituted with a member selected from the alkenyl, haloalkenyl, or alkynyl group include, 4-methylhept-4-en-1-yn-3-ol, 4-fluorohex-4-en-1-yn-3-ol and the like.

Specific examples of the alcohol compound of formula (3), 25 wherein R⁶ represents a methyl or ethyl group substituted with the heterocyclic group which may be substituted as defined above, include, for example, 2-furylmethyl alcohol, 3-furylmethyl alcohol, (5-phenoxy-3-furyl)methyl alcohol,

(5-benzyl-3-furyl)methane-1-ol,

{5-(difluoromethyl)-3-furyl)methane-1-ol,

5-propargylfurfuryl alcohol,

(5-methylisoxazole-3-yl)methane-1-ol,

5 1-{2-(trifluoromethyl)-1,3-thiazole-4-yl}prop-2-yn-1-ol,

1-{2-(trifluoromethoxy)-1,3-thiazole-4-yl}prop-2-yn-1-ol,

1-{1-prop-2-ynyl-5-(trifluoromethyl)pyrrole-3-yl}prop-2-yn-1-ol,

(1-prop-2-ynylpyrrole-3-yl)methane-1-ol,

10 3-(hydroxymethyl)-1-propynyl-imidazolidine-2,4-dione,

2-(hydroxymethyl)-4,5,6,7-tetrahydroisoindole-1,3-dione,

{1-(2-propynyl)pyrrole-3-yl)methane-1-ol,

5-(hydroxymethyl)-4-methyl-(2-propynyl)-1,3-thiazoline-2-one,

15 (1-prop-2-ynyl-2-methylindole-3-yl)methane-1-ol,

{1-prop-2-ynyl-2-(trifluoromethyl)indole-3-yl)methane-1-ol,

(2,3,6-trifluoro-4-pyridyl)methane-1-ol,

and the like.

Specific examples of the alcohol compound of formula (3),

20 wherein R⁶ represents a methyl or ethyl group substituted with at least one member selected from the aryl group which may be substituted as defined above, a cyano group, or the alkynyl group, include, for example, aralkyl alcohols such as:

benzyl alcohol, 2-methyl-3-phenylbenzyl alcohol,

25 2,3,5,6-tetrafluorobenzyl alcohol,

2,3,5,6-tetrafluoro-4-methylbenzyl alcohol,

2,3,5,6-tetrafluoro-4-methoxybenzyl alcohol,

2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl alcohol,

2,3,5,6-tetrafluoro-4-propargylbenzyl alcohol,

2,3,5,6-tetrafluoro-4-(difluoromethyl)benzyl alcohol,
2,3,5,6-tetrafluoro-4-(difluoromethoxy)benzyl alcohol,
2,3,5,6-tetrafluoro-4-(2,2,2-trifluoroacetoxy)methyl-
benzyl alcohol,
5 4-(trifluoromethyl)benzyl alcohol,
2,3,4,5-tetrafluoro-6-methylbenzyl alcohol,
3-phenylbenzyl alcohol, 2,6-dichlorobenzyl alcohol,
3-phenoxybenzyl alcohol,
2-hydroxy-2-(3-phenoxyphenyl)ethanenitrile,
10 2-hydroxy-2-{4-(methoxymethyl)phenyl}ethanenitrile,
2-{3-(4-chlorophenoxy)phenyl}-2-hydroxyethanenitrile,
2-(4-amino-2,3,5,6-tetrafluorophenyl)-2-hydroxyethane-
nitrile,
2-(4-fluoro-3-phenoxyphenyl)-2-hydroxyethanenitrile,
15 (2-methylphenyl)methyl alcohol,
(3-methylphenyl)methyl alcohol,
(4-methylphenyl)methyl alcohol,
(2,3-dimethylphenyl)methyl alcohol,
(2,4-dimethylphenyl)methyl alcohol,
20 (2,5-dimethylphenyl)methyl alcohol,
(2,6-dimethylphenyl)methyl alcohol,
(3,4-dimethylphenyl)methyl alcohol,
(2,3,4-trimethylphenyl)methyl alcohol,
(2,3,5-trimethylphenyl)methyl alcohol,
25 (2,3,6-trimethylphenyl)methyl alcohol,
(3,4,5-trimethylphenyl)methyl alcohol,
(2,4,6-trimethylphenyl)methyl alcohol,
(2,3,4,5-tetramethylphenyl)methyl alcohol,
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Preferred monohydroxy compound (3) are primary alcohols, such as benzyl alcohol, pentafluoroethyl alcohol, 3,3-dibromo-2-propene-1-ol, perfluoropropyl alcohol, hexafluoroisopropyl alcohol, perfluorobutyl alcohol, 5 perfluoropentyl alcohol, perfluorohexyl alcohol, perfluoroctyl alcohol, perfluorodecyl alcohol, {1-(2-propynyl)-5-(trifluoromethyl)-4-pyrazolyl)methane-1-ol,

1-{1-(2-propynyl)-5-(trifluoromethyl)pyrrole-3-yl}prop-2-10 yn-1-ol,

1-{2-(trifluoromethyl)-1,3-thiazole-4-yl}prop-2-yn-1-ol,

1-{2-(trifluoromethoxy)-1,3-thiazole-4-yl}prop-2-yn-1-ol,

and 4-fluorohex-4-en-1-yn-3-ol.

Preferred are aralkyl alcohols and

15 hydroxycyclopentenones, and more preferred are:

3-phenoxybenzyl alcohol;

4-hydroxy-3-methyl-2-(2-propenyl)-2-cyclopentene-1-one; and

4-hydroxy-3-methyl-2-(2-propynyl)-2-cyclopentene-1-one.

An asymmetric center(s) may be present in the monohydroxy 20 compound (3), and any optical isomer or a mixture thereof may be used in the present process to produce an optically active desired ester(s) (1) with retention of configuration with respect to the asymmetric center(s) in the alcohol moiety.

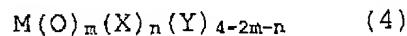
The monohydroxy compound (3) may be used in excess.

25 Preferably, the monohydroxy compound (3) is used 1 mol or less per mol of the cyclopropanecarboxylic acids (2). After completion of the reaction, unreacted materials may generally be recovered by such operation as distillation, extraction, or the like.

Next, a description will be made to the catalyst compound comprising an element of Group 4 of the Periodic Table of Elements.

Examples of the catalyst compound include a zirconium compound, a titanium compound, a hafnium compound and the like.

Preferred catalyst compounds are zirconium, titanium, and hafnium compounds having Lewis acidity, and can be represented by formula (4):



wherein M represents an element of Group 4 of the Periodic Table of Elements; X and Y independently represent a halogen atom, an alkoxy group, an acetylacetone group, an acyloxy group, an amino group which may be substituted with up to two alkyl groups, or a cyclopentadienyl group; and m is equal to 0 or 1, and n is equal to 0, 1, or 2.

Specific examples of the titanium and hafnium compounds include, for example, titanium halide such as titanium tetrafluoride, titanium tetrachloride, titanium tetrabromide, titanium tetraiodide; titanium acetate, titanium acetylacetone, titanium ethoxide, titanium i-propoxide, titanium n-butoxide, titanium t-butoxide; titanium oxychloride; titanium amide such as tetrakis(dimethylamino)titanium, tetrakis(diethylamino)titanium or the like; titanocene dichloride, titanocene dimethoxide, decamethyltitanocene dichloride; hafnium halide such as hafnium tetrafluoride, hafnium tetrachloride, hafnium tetrabromide, hafnium tetraiodide or the like; hafnium acetate, hafnium acetylacetone, hafnium alkoxide such as hafnium ethoxide,

hafnium i-propoxide, hafnium n-butoxide, hafnium t-butoxide or the like; hafnium oxychloride; amide compound of hafnium such as tetrakis(dimethylamino)hafnium, tetrakis(diethylamino)hafnium or the like; hafnocene 5 dichloride, hafnocene dimethoxide, and decamethylhafnocene dichloride.

Among the specific compounds, preferred are titanium tetrachloride, titanium i-propoxide, titanocene dichloride, hafnium tetrachloride, hafnium t-butoxide, and hafnocene 10 dichloride.

Specific examples of the zirconium compound includes, for example, zirconium halide such as zirconium tetrafluoride, zirconium tetrachloride, zirconium tetrabromide, zirconium tetraiodide or the like; zirconium acetate, zirconium acetylacetone; zirconium alkoxide such as zirconiummethoxide, zirconium i-propoxide, zirconium n-butoxide, zirconium t-butoxide or the like; zirconium oxychloride; amide compound of zirconium such as tetrakis(dimethylamino)zirconium, tetrakis(diethylamino)zirconium or the like; zirconocene 15 compound such as zirconocene dichloride, zirconocene dimethoxide, and decamethylzirconocene dichloride. Preferably are zirconium tetrachloride, zirconium t-butoxide, and zirconocene dichloride.

The compound comprising an element of Group 4 of the Periodic 25 Table of Elements may be used as commercially available anhydride or hydrate without any processing. A complex comprising a compound comprising an element of Group 4 of the Periodic Table of Elements and a compound having a ligating property such as tetrahydrofuran and tetramethylethylenediamine may also be

used.

Although any amount of the compound comprising an element of Group 4 of the Periodic Table of Elements may be used, it is normally catalytic and preferably around 0.001 to 200 mole % 5 permol of the cyclopropanecarboxylic acid (2), more preferably within the range of around 0.1 to 20 mole %, and still more preferably within the range of around 0.1 to 10 mole %.

The reaction of the cyclopropanecarboxylic acids (2) with the monohydroxy compound (3) in the presence of the catalyst 10 of the present invention is usually conducted in an inert gas atmosphere such as argon and nitrogen. The reaction may be performed under a normal pressure, a pressurized pressure, or a reduced pressure. Preferably, the reaction is performed under a normal pressure or a reduced pressure. In addition, it is 15 preferable to perform reaction while continuously removing water, which is formed as a byproduct of dehydration reaction, from the reaction system by such a method as distillation or the like.

The reaction may be performed in the absence of a solvent or in a solvent. The solvent that may be used includes: 20 halogenated hydrocarbons such as dichloromethane, chloroform, and 1,2-dichloroethane, aliphatic hydrocarbons such as hexane, heptane, octane, nonane or the like; aromatic hydrocarbons such as benzene, toluene, xylene, chlorobenzene or the like; and ether solvents such as diethyl ether, tetrahydrofuran or the like. 25 By-produced water may be removed from the reaction system by using a solvent that forms an azeotrope with the byproduct water.

Although a reaction temperature is not particularly defined, it is preferably within a range of around 20 to around 200 °C.

The catalyst may be removed by washing the reaction mixture with water or acidic water makes, and the cyclopropanecarboxylate esters (1) can be isolated by performing normal operation such as distillation, recrystallization, and column chromatography, 5 if necessary, from the reaction mixtures.

Examples

The present invention will be described in detail with the following examples, but it is not to be construed that the 10 present invention is limited to the examples.

Example 1

In a 10 ml test tube-type reactor, 0.43 g of 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid (E/Z=80/20), 0.50 g of 3-phenoxybenzyl alcohol, 5.8 mg of zirconium tetrachloride, and 5 ml of xylene were charged. 15 The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours at 145 °C while water generated as a by-product during reaction 20 was being separated and collected in the trap. A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 98% (E/Z=84/16, selectivity: 99%) based on the material 25 alcohol.

Example 2

The reaction was performed in a similar manner as in Example 1 except that 9.4 mg of a complex of zirconium tetrachloride

with 2-tetrahydrofuran was charged instead of 5.8 mg of zirconium tetrachloride in Example 1.

A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 95% (E/Z=85/15, selectivity: 98%) based on the material alcohol.

Example 3

10 The reaction was performed in a similar manner as in Example 1 except that 7.3 mg of zirconocene dichloride was charged instead of 5.8 mg of zirconium tetrachloride in Example 1.

A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 97% (selectivity: 98%) based on the material alcohol.

Example 4

20 The reaction was performed in a similar manner as in Example 1 except that 9.6 mg of zirconium t-butoxide was charged instead of 5.8 mg of zirconium tetrachloride in Example 1.

A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 91% (selectivity: 92%) based on the material alcohol.

Example 5

The reaction was performed in a similar manner as in Example 1 except that 6.6 mg of zirconium acetate was charged instead of 5.8 mg of zirconium tetrachloride in Example 1.

A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 95% (selectivity: 96%) based on the material alcohol.

10 Example 6

The reaction was performed in a similar manner as in Example 1 except that 0.47 g of (5-benzyl-3-furyl)methane-1-ol was charged instead of 0.50 g of 3-phenoxybenzyl alcohol in Example 1.

15 A reaction mixture thereof was analyzed with gas chromatography to find that (5-benzyl-3-furyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 92% (selectivity: 99%) based on the material alcohol.

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Comparative Example 1

The reaction was performed in a similar manner as in Example 1 except that 12.5 mg of concentrated sulfuric acid was charged instead of 5.8 mg of zirconium tetrachloride in Example 1.

25 A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 81% (selectivity: 87%) based on the material alcohol.

Comparative Example 2

The reaction was performed in a similar manner as in Example 1 except that 23.7 mg of p-toluenesulfonic acid was charged 5 instead of 5.8 mg of zirconium tetrachloride in Example 1.

A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 61% (selectivity: 93%) based on the 10 material alcohol.

Example 7

In a 10 ml test tube-type reactor, 0.43 g of 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic 15 acid, 0.38 g of 4-hydroxy-3-methyl-2-(2-propenyl)-2-cyclopentene-1-on, 48.0 mg of zirconium t-butoxide, and 5 ml of xylene were charged. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours 20 at 145°C while water generated as a by-product during reaction was being separated and collected in the trap. A reaction mixture thereof was analyzed with gas chromatography to find that 3-(2-propenyl)-2-methyl-4-oxo-2-cyclopentenyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxyl- 25 ate was obtained in a yield of 62% (selectivity: 97%) based on the material alcohol.

Example 8

In a 10 ml test tube-type reactor, 0.85 g of 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid, 0.75 g of 4-hydroxy-3-methyl-2-(2-propenyl)-2-cyclopentene-1-on, 58 mg of zirconium tetrachloride, and 5 ml of xylene were charged. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 16 hours at 145°C while water generated as a by-product during reaction was being separated and collected in the trap. A reaction mixture thereof was analyzed with gas chromatography to find that 3-(2-propenyl)-2-methyl-4-oxo-2-cyclopentenyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 85% (selectivity: 90%) based on the material alcohol.

15 Examples 9 to 11

Experiments were conducted in a similar manner as in Example 8 except that the following alcohol compounds and the zirconium compounds were used in place of the alcohol and zirconium compounds used in Example 8.

Ex.	Alcohol compound	Zirconium compound	Yield(%) of ester	Selectivity (%)
9	A	Zr[OCH(CH ₃) ₂] ₄ 82 mg	94	94
10	B 0.75 g	ZrCl ₄	87	87
11	B 0.75 g	Zr[OCH(CH ₃) ₂] ₄ 82 mg	93	97

A: 4-hydroxy-3-methyl-2-(2-propenyl)-2-cyclopentene-1-on

B: 4-hydroxy-3-methyl-2-(2-propynyl)-2-cyclopentene-1-on

Example 12

In a 10 ml test tube-type reactor, 0.16 g of 2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylic acid, 0.22 g of 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl alcohol, 3.3 mg of zirconium tetrakisopropoxide, and 5 ml of xylene were charged. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours at 145 °C while water generated as a by-product during reaction was being separated and collected in the trap. A reaction mixture thereof was analyzed with gas chromatography to find that 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl 2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylate was obtained in a yield of 83% (selectivity: 98%) based on the material alcohol.

15 Example 13

In a 10 ml test tube-type reactor, 0.34 g of 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid, 0.45 g of 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl alcohol, 4.7 mg of zirconium tetrachloride, and 5 ml of xylene were charged. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours at 145 °C while water generated as a by-product during reaction was being separated and collected in the trap. A reaction mixture thereof was analyzed with gas chromatography to find that 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 68% (selectivity: 98%) based on the material alcohol.

Examples 14 to 18

Experiments were conducted in a similar manner as in Example 13 except that following zirconium compounds and amounts.

Ex.	Zirconium compound	Yield of ester (%)	Selectivity (%)
14	(ZrCl ₄) 9.3 mg	92	98
15	ZrBr ₄ 8.2 mg	62	96
16	ZrCl ₄ THF complex 7.5 mg	78	99
17	Zr[OCH(CH ₃) ₂] ₄ 6.5 mg	74	97
18	Zirconocene dichloride, 8.8 mg	63	99

5

Example 19

In a 10ml test tube-type reactor, 0.43 g of 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid, 0.50 g of 3-phenoxybenzyl alcohol, 8.0 mg of hafnium

10 tetrachloride, and 5 ml of xylene were charged. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours at 145 °C while water generated as a by-product during reaction was being separated and collected in the trap. A reaction mixture 15 thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 86% (selectivity: 94%) based on the material alcohol.

20 Example 20

The reaction was performed in a similar manner as in Example

19 except that 11.6 mg of a hafnium tetrachloride-2 tetrahydrofuran complex was charged instead of 8.0 mg of hafnium tetrachloride in Example 19.

5 A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 97% (selectivity: 98%) based on the material alcohol.

10 Example 21

The reaction was performed in a similar manner as in Example 19 except that 12.0 mg of a hafnium tetrachloride-2pyridine complex was charged instead of 8.0 mg of hafnium tetrachloride in Example 19.

15 A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 96% (selectivity: 98%) based on the material alcohol.

20

Example 22

The reaction was performed in a similar manner as in Example 19 except that 12.5 mg of a hafnium tetrabromide was charged instead of 8.0 mg of hafnium tetrachloride in Example 19.

25 A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 87% (selectivity: 93%) based on the material alcohol.

Example 23

The reaction was performed in a similar manner as in Example 19 except that 10.5 mg of pentamethylcyclopentadienylhafnium trichloride was charged instead of 8.0 mg of hafnium tetrachloride in Example 19.

A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 90% (selectivity: 94%) based on the material alcohol.

Example 24

The reaction was performed in a similar manner as in Example 19 except that 8.9 mg of tetrakis(diethylamino) hafnium was charged instead of 8.0 mg of hafnium tetrachloride in Example 19. A reaction mixture thereof was analyzed with gas chromatography, and the result indicated that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 93% (selectivity: 99%) based on the material alcohol.

Comparative Example 3

The reaction was performed in a similar manner as in Example 19 except that 12.5 mg of concentrated sulfuric acid was prepared instead of 8.0 mg of hafnium tetrachloride in Example 19. A reaction mixture thereof was analyzed with gas chromatography to find that (3-phenoxyphenyl)methyl

2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 81% (selectivity: 87%) based on the material alcohol.

5 Comparative Example 4

The reaction was performed in a similar manner as in Example 19 except that 23.7 mg of p-toluenesulfonic acid was charged instead of 8.0 mg of hafnium tetrachloride in Example 19. A reaction mixture thereof was analyzed with gas chromatography

10 to find that (3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 61% (selectivity: 93%) based on the material alcohol.

15 Example 25

In a 10 ml test tube-type reactor were charged 0.43 g of 2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropanecarboxylic acid, 0.38 g of 4-hydroxy-3-methyl-2-(2-propenyl)-2-cyclopentene-1-one, 58.1 mg of a hafnium tetrachloride-2tetrahydrofuran complex, and 5 ml of xylene. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours at 145 °C while water generated as a by-product during reaction was being separated and collected in the trap. The resulting reaction mixture was analyzed with gas chromatography to find that 3-(2-propenyl)-2-methyl-4-oxo-2-cyclopentenyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 65% (selectivity: 84%) based on the material alcohol

Example 26

The reaction was performed in a similar manner as in Example 25 except that 62.1 mg of a hafnium tetrachloride·2dioxane complex was charged instead of 58.1 mg of a hafnium tetrachloride·2 tetrahydrofuran in Example 25. A reaction mixture thereof was analyzed with gas chromatography to find that 3-(2-propenyl)-2-methyl-4-oxo-2-cyclopentenyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 59% (selectivity: 80%) based on the material alcohol.

Comparative Example 5

The reaction was performed in a similar manner as in Example 25 except that 12.5 mg of concentrated sulfuric acid was charged instead of 58.1 mg of a hafnium tetrachloride·2 tetrahydrofuran complex in Example 25. A reaction mixture thereof was analyzed with gas chromatography to find that 3-(2-propenyl)-2-methyl-4-oxo-2-cyclopentenyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 30% (selectivity: 31%) based on the material alcohol.

Comparative Example 6

Reaction was performed in a similar manner as in Example 25 except that 23.7 mg of p-toluenesulfonic acid was charged instead of 58.1 mg of a hafnium tetrachloride·2 tetrahydrofuran complex in Example 25. A reaction mixture thereof was analyzed with gas chromatography to find that

3-(2-propenyl)-2-methyl-4-oxo-2-cyclopentenyl
2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
was obtained in a yield of 6.4% (selectivity: 8%) based on the
material alcohol.

5

Example 27

In a 10ml test tube-type reactor, there were prepared 0.43
g of 2,2-dimethyl-3-(2-methyl-1-propenyl)
cyclopropanecarboxylic acid, 0.38 g of 4-hydroxy-3-methyl-2-
10 (2-propynyl)-2-cyclopentene-1-one, 58.1 mg of a complex made
of hafniumtetrachloride and 2-tetrahydrofuran, and 5ml of xylene
were charged. The reactor was equipped with a Dean-Stark trap
and a condenser, and the reaction mixture was stirred under reflux
for 8 hours at 145 °C while water generated as a by-product during
15 reaction was being separated and collected in the trap. A
reaction mixture thereof was analyzed with gas chromatography
to find that 3-(2-propynyl)-2-methyl-4-oxo-2-cyclopentenyl
2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
was obtained in a yield of 61% (selectivity: 79%) based on the
20 material alcohol.

Example 28

The reaction was performed in a similar manner as in Example
27 except that 62.1 mg of a hafnium tetrachloride-2dioxane
25 complex was charged instead of 58.1 mg of a hafnium
tetrachloride-2tetrahydrofuran complex in Example 27.

A reaction mixture thereof was analyzed with gas
chromatography to find that 3-(2-propynyl)-
-2-methyl-4-oxo-2-cyclopentenyl 2,2-dimethyl-3-

(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 58% (selectivity: 79%) based on the material alcohol.

Comparative Example 7

5 The reaction was performed in a similar manner as in Example 27 except that 12.5 mg of concentrated sulfuric acid was charged instead of 58.1 mg of a hafnium tetrachloride·2tetrahydrofuran complex in Example 27.

10 A reaction mixture thereof was analyzed with gas chromatography to find that 3-(2-propynyl)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 9.3% (selectivity: 12%) based on the material alcohol.

15 Comparative Example 8

The reaction was performed in a similar manner as in Example 27 except that 23.7 mg of p-toluenesulfonic acid was charged instead of 58.1 mg of a hafnium tetrachloride·2tetrahydrofuran complex in Example 27.

20 A reaction mixture thereof was analyzed with gas chromatography to find that 3-(2-propynyl)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 0.8% (selectivity: 4.4%) based on the material alcohol.

25

Example 29

In a 10 ml test tube-type reactor, 0.16 g of 2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylic acid, 0.22 g of 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl alcohol, 4.6

mg of a hafnium tetrachloride·2tetrahydrofuran complex, and 5 ml of xylene were charged. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours at 145°C while water generated
5 as a by-product during reaction was being separated and collected in the trap. A reaction mixture thereof was analyzed with gas chromatography to find that
2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl
2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylate was
10 obtained in a yield of 80% (selectivity: 99%) based on the material alcohol.

Example 30

The reaction was conducted in a similar manner as in Example
15 29 except that 5.0 mg of hafnium tetrabromide was used in place of 4.6 mg of a hafnium tetrachloride·2tetrahydrofuran complex. Analysis of the reaction mixture showed that the yield of 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl
2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylate was 95%
20 (selectivity: 97%) based on the alcohol.

Example 31

In a 10 ml test tube-type reactor, 0.34 g of 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid, 0.45 g of 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl alcohol, 18.6 mg of a hafnium tetrachloride·2tetrahydrofuran complex, and 5 ml of xylene were charged. The reactor was equipped with a Dean-Stark trap and a condenser, and the reaction mixture was stirred under reflux for 8 hours at 145°C while water

generated as a by-product during reaction was being separated and collected in the trap. A reaction mixture thereof was analyzed with gas chromatography to find that 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl
5 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate was obtained in a yield of 70% (selectivity: 99%) based on the material alcohol.

Example 32

10 The reaction was conducted in a similar manner as in Example 31 except that 19.9 mg of hafnium tetrabromide was used in place of 18.6 mg of a hafnium tetrachloride·2tetrahydrofuran complex. Analysis of the reaction mixture showed that the yield of 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl
15 2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylate was 81% (selectivity: 87%) based on the alcohol.